[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

No. 34,878, A.D. 1930.

Improvements in or relating to the Refining of Oils.

We, MURRAY STUART, D.Sc., Ph.D., M.Inst.P.T., a British Subject, of Dashwood House, 69, Old Broad Street, London, E.C. 2, and LEWIS MURRAY STUART, a British Subject, of 78, Lord Street, Liverpool, Lancashire, do hereby declare the nature of this invention to be as follows:—

This invention is for improvements in or relating to the refining of oils and has particular reference to the treatment of oils consisting wholly or mainly of hydrocarbons. Such oils include petroleum, synthetic and hydrogenated oils and the oils obtained by the distillation of coal, lignite, carbonaceous shale, peat, torbanite and the like. It is well known that oils such as those just mentioned contain in addition to liquid hydrocarbons varying amounts of undesirable constituents including compounds containing combined sulphur, dissolved bitumens and unsaturated hydrocarbons which are liable to oxidize or polymerize to form products of a gummy or resinous nature.

It has been proposed to remove uncombined sulphur and carbon from hydrocarbons by oxidizing these substances to their gaseous oxides with ozone or with a mixture of ozone and air or ozone and oxygen. Oxidation of a sufficiently vigorous character to oxidize free carbon or sulphur leads also to the oxidation of a large proportion of the unsaturated constituents of the oil, and as unsaturated hydrocarbons form a not inconsiderable proportion of the oils obtained by the distillation of carbonaceous materials or by cracking processes, it is a matter of importance to prevent undue loss of this portion of the product.

We have found that an oxidizing agent consisting of ozonized air (as distinct from ozone mixed with air) prepared by the usual type of air ozonizer is sufficiently powerful to oxidize combined sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins while leaving free sulphur and carbon and the more stable unsaturated hydrocarbons unattacked. The oxidized products are effectively removed from the oils by processes of washing and distillation. The present invention accordingly consists in a process for refining hydrocarbon oils which comprises treating the hydrocarbon oil with ozonised air so as to oxidise sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins without oxidising free sulphur and free carbon and subsequently washing the oil with an aqueous alkaline solution and distilling.

The oil may be sprayed into the ozonised air or the ozonised air may be blown through the oil. In one convenient form of apparatus the oil descending a bubble tower is treated with an ascending current of ozonised air.

The ozonised air treatment leads to the conversion of sulphur-containing compounds such as mercaptans, alkyl sulphides and disulphides, thiophenes and thiophanes into oxidised products which are soluble in aqueous alkaline solutions while the bitumens and the unsaturated hydrocarbons which oxidise or polymerise into gums and resins form products which precipitate from the oil before or are extracted from solution in the oil during the alkaline washing, or form compounds of high boiling point from which the oils are removed during the subsequent distillation.

If desired, the oil after treatment with the ozonised air and before washing may be filtered.

The aqueous alkaline solution for washing the oil may comprise for example a solution of sodium hydrate, sodium carbonate or preferably a solution of calcium hydrate, and the method of separating the oil from the aqueous liquid prior to distilling the former may be any one of the well known processes employed in the oil industry.

The chamber in which the oxidizing treatment takes place may be heated or the oil may be passed into it in the vapour

[*Price* 1/-].

phase. It is desirable to take precautions to ensure that the oils undergoing the oxidizing treatment are free from moisture.

The oxidizing step of the process of refining is usually carried out under atmospheric pressure but it will be appreciated that the temperature and pressure adopted in the treatment of any particular oil will depend upon the nature and amount of oxidizable impurities present and that these last mentioned factors will also govern the concentration of the ozone required in the ozonized air, the proportion of ozonized air to oil and the time during which the air and oil are permitted to remain in contact. It will be clear from the foregoing that a knowledge of the main impurities to be removed from any particular sample of oil is essential to success and that a simple preliminary test is in most cases advisable.

This invention finds application not only in the refining of crude oils but also in the treatment of the fractions obtained from them. When applied to those fractions yielding lubricating oils it is found that in addition to removing undesirable constituents the treatment results in an increase in viscosity which enhances the value of the product.

Dated this 19th day of November, 1930.

BOULT, WADE & TENNANT,
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PROVISIONAL SPECIFICATION.

No. 22,784, A.D. 1931.

Improvements in or relating to the Refining of Oils.

We, MURRAY STUART, D.Sc., Ph.D., M.Inst.P.T., a British Subject, of Dashwood House, 69, Old Broad Street, London, E.C. 2, and LEWIS MURRAY STUART, a British Subject, of 78, Lord Street, Liverpool, Lancashire, do hereby declare the nature of this invention to be as follows:—

This invention is for improvements in or relating to the refining of oils and has particular reference to the treatment of oils consisting wholly or mainly of hydrocarbons.

In our co-pending Application No. 31,873/30 we have described the purification of oils by treatment with ozonised air so as to oxidize sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins without oxidizing free sulphur and free carbon and subsequently washing the oil with an aqueous alkaline solution and distilling.

We have now found that while this treatment is effective in converting certain gum and resin-forming constituents into easily removable products it is advantageous in the case of other gum and resin-forming substances which are less amenable to treatment, to employ a catalyst, condensing agent or contact substance or mixture of catalysts, condensing agents, or contact substances, in conjunction with the ozonized air treatment.

According to the present invention there is provided a process for refining hydrocarbon oils which comprises treating the oil with ozonized air in the presence of a catalyst, condensing agent or contact substance, or mixture of catalysts, condensing agents, or contact substances, so as to convert sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins into products which are readily removable without oxidizing free sulphur and free carbon and subsequently washing the oil with an aqueous alkaline solution and distilling.

In certain cases the treatment of the oil with catalysts or contact agents may with advantage follow the treatment with ozonized air and this is particularly advisable in those cases in which conversion of gum or resin-forming substances in the presence of a catalyst or catalysts only takes place at such elevated temperatures as would lead to the thermal decomposition of ozone.

Among the catalysts, condensing agents or contact substances suitable for use in the present process may be mentioned sulphuric acid, the chlorides or sulphates of heavy metals for example zinc chloride, iron chloride, iron sulphate, tin chloride or copper sulphate. Fullers earth "floridin", or bauxite may also be used and the oil in the liquid or vapour phase may be passed through the catalyst.

According to a modified form of treatment the oil is acted upon during or after treatment with ozonized air with a mixture of a salt of a heavy metal (for example iron chloride or iron sulphate) and sulphuric acid in such concentration as to convert the potertial gum-forming compounds but to leave unattacked unsaturated hydrocarbons which do not give rise to gums and resins.

It will be understood that the most

efficient catalyst for the treatment of any particular oil will depend on the precise nature of the potential gum or resin-forming materials which it is desired to remove and a simple test will indicate what catalyst or mixture of catalysts will be most effective.

Dated this 12th day of August, 1931.

BOULT, WADE & TENNANT,
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COMPLETE SPECIFICATION.

Improvements in or relating to the Refining of Oils.

We, MURRAY STUART, D.Sc., Ph.D., M.Inst.P.T., a British Subject, of Dashwood House, 69, Old Broad Street, London, E.C. 2, and LEWIS MURRAY STUART, a British Subject, of 78, Lord Street, Liverpool, Lancashire, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement: —

This invention is for improvements in or relating to the refining of the various fractions obtained by the distillation of crude oils consisting wholly or mainly of hydrocarbons. Such oils include petroleum, synthetic and hydrogenated oils and the oils obtained by the distillation of coal, lignite, carbonaceous shale, peat, torbanite and the like and the products obtained by cracking such oils. It is well known that oils such as those just mentioned contain in addition to liquid hydrocarbons varying amounts of compounds containing combined sulphur, dissolved bitumens and certain unsaturated hydrocarbons which are liable to oxidise or polymerise to form products of a gummy or resinous nature and these unstable materials pass over into the fractions obtained from the crude oils by processes of distillation or cracking. It will be understood that such polymerisable unsaturated compounds while not objectionable in themselves are undesirable in oils which are to be stored for any length of time as under these circumstances gummy or resinous products are formed from them. As gummy or resinous materials are highly undesirable in most distilled oil fractions particularly in the more volatile and the lubricating oil fractions it is a matter of some importance to remove the gum-forming unsaturated compounds from these fractions by a method which is both simple and effective. It has been proposed to remove uncombined sulphur and carbon from hydrocarbons by oxidising these substances to their gaseous oxides with ozone or with ozonized air or ozonized oxygen. Oxidation of a sufficiently vigorous character to oxidise free carbon or sulphur leads also to the oxidation of a large proportion of the unsaturated constituents of the oil, and as unsaturated hydrocarbons form a not inconsiderable proportion of the oils obtained by the distillation of carbonaceous materials or by cracking processes, it is a matter of importance to prevent undue loss of this portion of the product.

We have found that an oxidising agent consisting of ozonized air prepared by the usual type of air ozonizer is sufficiently powerful to oxidize combined sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins while leaving free sulphur and free carbon and the more stable unsaturated hydrocarbons unattached. The oxidized products are effectively removed from the oils by processes of washing and distillation. The present invention accordingly consists in a process for refining oil fractions obtained by the distillation of hydrocarbon oils which comprises treating the hydrocarbon oil fraction with ozonized air so as to oxidize sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins without oxidizing free sulphur and free carbon and subsequently washing the oil with an aqueous alkaline solution and distilling. It is advantageous in the case of certain oils which contain gum and resin-forming substances which are less amenable to treatment, to employ a catalyst, condensing agent or contact substance or mixture of catalysts, condensing agents, or contact substances, in conjunction with the ozonized air treatment, and this invention further consists in a process in which the treatment with ozonized air is accompanied by or followed by a treatment with a catalyst, condensing agent or contact substance or with a mixture of catalysts, condensing agents or contact substances and the oil is subsequently washed with an aqueous alkaline solution and distilled. This catalyst, condensing agent or contact substance is a

substance such as a salt of a heavy metal (for example iron chloride or iron sulphate) or sulphuric acid, or Fullers earth, "floridin", or bauxite which polymerises the gum-forming compounds but leaves unattacked those unsaturated hydrocarbons which do not give rise to gums and resins.

The treatment of the oil with catalysts condensing agents or contact substances may with advantage follow the treatment with ozonised air and this is particularly advisable in those cases in which conversion of gum or resin-forming substances in the presence of a catalyst or catalysts only takes place at such elevated temperatures as would lead to the thermal decomposition of ozone.

Among the catalysts, condensing agents or contact substances suitable for use in this modification of the present process may be mentioned sulphuric acid, the chlorides or sulphates of heavy metals for example zinc chloride, iron chloride, iron sulphate or persulphate, tin chloride or copper sulphate. Further, a salt of a heavy metal (for example iron chloride or iron sulphate) together with sulphuric acid in such quantity and concentration or dilution as to convert the potential gum-forming compounds but to leave unattacked unsaturated hydrocarbons which do not give rise to gums and resins may be employed. Fullers earth, "floridin" or bauxite may also be used and the oil in the liquid or vapour phase may be passed through the catalyst.

The precise nature of the reactions which take place when oil fractions are treated with ozonized air in accordance with this invention is doubtful.

The oil fractions to be treated may be sprayed into the ozonized air or the ozonized air may be blown through the oil. In one convenient form of apparatus the oil descending a bubble tower is treated with an ascending current of ozonized air. The treatment with ozonized air may if desired be carried out under reduced pressure.

The ozonized air treatment leads to the conversion of sulphur-containing compounds such as mercaptans, alkyl sulphides and disulphides, thiophenes and thiophanes into oxidized products which are soluble in aqueous alkaline solutions while the bitumens and the unsaturated hydrocarbons which oxidize or polymerize into gums and resins from products which precipitate from the oil before or are extracted from solution in the oil during the alkaline washing, or form compounds of high boiling point from which the oils are removed during the subsequent distillation.

If desired the oil, after treatment with the ozonized air and before washing may be filtered.

The aqueous alkaline solution for washing the oil may comprise for example a solution of sodium hydrate, sodium carbonate or preferably in some cases a solution of calcium hydrate, and the method of separating the oil from the aqueous liquid prior to distilling the former may be any one of the well-known processes employed in the oil industry.

The chamber in which the oxidizing treatment takes place may be heated or the oil may be passed into it in the vapour phase. It is desirable to take precautions to ensure that the oils undergoing the oxidizing treatment are free from moisture.

The oxidizing step of the process of refining is usually carried out under atmospheric pressure but it will be appreciated that the temperature and pressure adopted in the treatment of any particular oil will depend upon the nature and amount of oxidizable impurities present and that these last mentioned factors will also govern the concentration of the ozone required in the ozonized air, the proportion of ozonized air to oil and the time during which the air and oil are permitted to remain in contact. It will also be understood that in those modifications of the process in which catalytic materials are used the optimum amount of catalyst, condensing agent or contact substance and the optimum temperature and time of treatment will depend on the nature of the oil and its impurities. It will be clear from the foregoing that a knowledge of the main impurities to be removed from any particular sample of oil is essential to success and that a simple preliminary test is in most cases advisable.

When applied to those fractions yielding lubricating oils it is found that in addition to removing undesirable constituents the treatment results in an increase in viscosity which enhances the value of the product.

EXAMPLE.

Following is a description by way of example of one method of carrying the invention into effect.

A petroleum oil fraction containing as an impurity unsaturated compounds which by processes of oxidation and/or polymerisation form gums or resins is allowed to descend a bubble tower maintained at atmospheric temperature and is met by an ascending current of ozonized air produced in an ozonizer of usual form. The oil on reaching the foot of the tower is run into a still and is vaporised, the oil

vapour being passed up a vertical tower packed with "floridin" or other similar substance having a catalytic effect on the polymerisation of gum or resin-forming unsaturated compounds. The treated vapours are condensed and the oil filtered, washed with a solution of calcium hydrate and finally fractionated in apparatus of the usual type.

We make no claim to anything disclosed in Specifications Nos. 346,152; 8486/07; 22,430/06 and 17,371/99.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for refining oil fractions obtained by the distillation of hydrocarbon oils which comprises treating the oil fraction with ozonized air so as to oxidize sulphur compounds and those unsaturated compounds which are responsible for the formation of gums and resins without oxidizing free sulphur and free carbon and subsequently washing the oil with an aqueous alkaline solution and re-distilling.

2. A process for refining oil fractions obtained by the distillation of hydrocarbon oils as claimed in Claim 1 wherein the treatment with ozonized air is accompanied by or followed by a treatment with a catalyst, condensing agent or contact substance or with a mixture of catalysts, condensing agents or contact substances hereinbefore referred to and the oil is subsequently washed with an aqueous alkaline solution and re-distilled.

3. A process for refining oil fractions obtained by the distillation of hydrocarbon oils as claimed in Claim 1 or Claim 2 wherein the hydrocarbon oil is sprayed into ozonized air.

4. A process for refining oil fractions obtained by the distillation of hydrocarbon oils as claimed in any one of the preceding claims wherein the treatment with ozonized air alone or with the catalyst, condensing agent or contact substance takes place at an elevated temperature.

5. A process for refining oil fractions obtained by the distillation of hydrocarbon oils as claimed in Claim 4 characterised in that the hydrocarbon oil is vaporised and brought into contact with the catalyst, condensing agent or contact substance.

6. A process for refining oil fractions obtained by the distillation of hydrocarbon oils as claimed in any one of the preceding claims wherein the treatment with ozonized air is carried out under reduced pressure.

7. A process for refining oil fractions obtained by the distillation of hydrocarbon oils as claimed in any one of the preceding claims which includes the step of filtering the oil before treatment with the aqueous alkaline solution.

8. A process for refining oil fractions obtained by the distillation of hydrocarbon oils substantially as described in the specific example hereinbefore set forth.

9. Oil fractions obtained by the distillation of hydrocarbon oils whenever purified by the process claimed in any one of the preceding claims.

Dated this 17th day of August, 1931.

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Reference has been directed, in pursuance of Section 7, Sub-section 4, of the Patents and Designs Acts, 1907 to 1928, to Specification No. 346,152.

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